

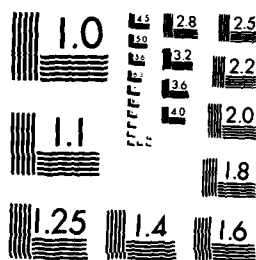
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OPTICAL ABSORPTION IN DOPED CDXHG1-XTE(U) ROYAL SIGNALS 1/1
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R G HUMPHREYS AUG 87 RSRE-MEMO-4069 DRIC-BR-103380

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AUTHOR R G Humphreys

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SUMMARY

The theory of optical absorption in heavily doped (degenerate) CMT is formulated to make use of the most recently measured band parameters. The absorption theory is compared with Anderson's approximation to Kane's k.p theory. The differences are found to be small near threshold, due to a somewhat fortuitous cancellation of errors. The dispersion of the refractive index near the band gap is calculated. This has only a small effect on the calculated absorption, but could be of importance in modelling interference fringes in thin detectors.



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RSRE MEMORANDUM 4069

OPTICAL ABSORPTION IN DOPED $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$

R G Humphreys

INTRODUCTION

The theory of the absorption of narrow gap semiconductors was first derived by Kane (1). In the intervening thirty years, various changes in notation and sophistication of the theory have occurred, and it is now not entirely straightforward to use modern band parameter data from the literature to deduce what the optical absorption coefficient should be. In addition, some publications (2,3) have made use of approximations to obtain absorption coefficients in a nearly analytic form. These are not easy to improve if experimental data fails to fit the theory. With the widespread availability of computers nowadays, it is often easier to use the exact theory than to approximate, and let the machine do the hard work.

The present work was undertaken to attempt to explain the temperature dependence of the absorption edge in heavily n-type $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ (CMT) which appeared to be anomalous. This is of some interest, as the temperature dependence of the band gap of CMT has never been explained (4) and the experiments could help to shed light on how the band parameters vary with temperature. The intention in this work, therefore, is to use the most accurate formulation of the theory and the most up to date band parameters to calculate both the absorption coefficient and the Fermi energy and its temperature dependence, so that if any discrepancy remains, this must indicate some inadequacy in the state of the art description of the band structure of heavily doped CMT.

THEORY

We shall not review here the various formulations of the band parameters. The most recent and most carefully thought out appear to be those of Weiler (5). Experience suggests that these may very well have deficiencies for two reasons. Firstly, they are based largely on interband rather than intraband magneto-optics. Such experiments are bedevilled by exciton corrections, and, so far as I am aware, these corrections have never been fully resolved for the classic narrow gap material, InSb. Secondly, such intraband experiments as are included in the analysis have been interpreted in terms only of energies calculated for zero momentum parallel to the field. This approach is well known to be inadequate. Even with these reservations, the band parameters are still probably as

reliable a set as are available. It is not made clear whether the parameters are supposed to apply at low energies (polaron corrected) or at high energies ($>\hbar\omega_{LO}$). I shall ignore this difficulty.

It does not seem sensible, in the light of these comments, to go to the extra complication of a full anisotropic calculation. The band parameters suggest that the anisotropy ($\gamma_3 - \gamma_2$) is not too large, as one would expect, and this work will use a spherical Hamiltonian which takes full account of non-parabolicity, but neglects band warping.

It is important when using a set of band parameters to understand which notation is being used. I shall take as the starting point the 8×8 Hamiltonian given by Weiler. This uses the Luttinger parameters, which include the effect of the free electron mass found in k.p theory (1). This is not so for the analogous conduction band parameter F . Since I assume that the band structure is spherical, it is sufficient to write the Hamiltonian for a single direction of k (k_z), in which case it yields a parabolic heavy hole band, with effective mass m^*

$$\frac{m_o}{m} = \gamma_1 - 2\gamma'$$

where γ' is the average value chosen to represent γ_2 and γ_3 in a spherical approximation. The remaining 3×3 Hamiltonian is

$$\begin{bmatrix} E_g + (F + \frac{1}{2}) \frac{\hbar^2 k^2}{m} & -\frac{\sqrt{2}}{\sqrt{3}} Pk & -\frac{1}{\sqrt{3}} Pk \\ -\frac{\sqrt{2}}{\sqrt{3}} Pk & -\left[\frac{\gamma_1}{2} - \gamma'\right] \frac{\hbar^2 k^2}{m} & -\sqrt{2}\gamma' \frac{\hbar^2 k^2}{m} \\ -\frac{1}{\sqrt{3}} Pk & -\sqrt{2}\gamma' \frac{\hbar^2 k^2}{m} & -\Delta - \frac{\gamma_1}{2} \frac{\hbar^2 k^2}{m} \end{bmatrix} \begin{bmatrix} a \\ b' \\ c' \end{bmatrix} = E \begin{bmatrix} a \\ b' \\ c' \end{bmatrix} \quad (1)$$

where the notation is mainly Weiler's. The eigenvector (a, b', c') denotes the contribution from the conduction band, light hole band and spin orbit split off band which are mixed into a given band away from $k = 0$. E is the energy eigenvalue for a given wavevector k . P is the interband matrix element, the γ 's are Luttinger parameters accounting for interactions with higher bands and F plays the same role for the conduction band. The matrix is written in practical units (ie incorporating k and m), and the matrix element P is in eVcm. The conversion from matrix elements squared (P^2) quoted in eV is achieved by multiplying them by $\hbar^2/2m$.

This form of the Hamiltonian is not very convenient for establishing a connection with Kane's theory for the absorption. It is straightforward to transform the matrix into the basis used by Kane, which makes the similarity more apparent. The matrix becomes.

$$\begin{bmatrix} E_g + (F+\frac{1}{2}) \frac{\hbar^2 k^2}{m} & 0 & kP \\ 0 & -\frac{2\Delta}{3} - \left[\frac{\gamma_1}{2} - \gamma' \right] \frac{\hbar^2 k^2}{m} & \frac{\sqrt{2}\Delta}{3} \\ kP & \frac{\sqrt{2}\Delta}{3} & -\frac{\Delta}{3} - \left[\frac{\gamma_1}{2} + 2\gamma' \right] \frac{\hbar^2 k^2}{m} \end{bmatrix} \quad (2)$$

The secular equation, whose solutions are the eigenvalues E is easy to write down in a form analogous to Kane's equation 10. It is no longer so easy to solve analytically because of the extra terms in k . It remains easy to solve numerically. The eigenfunctions (Kane's parameters a , b and c) are then straightforwardly obtained by matrix arithmetic;

$$\begin{aligned} a &= +kP \left[E + \frac{2\Delta}{3} + \gamma_1 k^2 - \gamma' k^2 \right] / N \\ b &= \frac{\sqrt{2}\Delta}{3} \left[E - E_g - (F+\frac{1}{2}) k^2 \right] / N \\ c &= \left[E - E_g - (F+\frac{1}{2}) k^2 \right] \left[E + \frac{2\Delta}{3} + \gamma_1 k^2 - \gamma' k^2 \right] / N \end{aligned} \quad (3)$$

where N is a normalizing factor equal to the square root of the sum of the squares of the numerators. The form of these expressions is the same as those of Kane. These lead directly to the absorption coefficient, as in Kane's paper. His equation 35 is quoted without reference. It is perhaps worth pointing out that this equation is essentially the same as that given by Schiff (equation 44.17, ref 6) with the refractive index deriving from the reduced electric field which corresponds to a given photon flux in a medium. In using the eigenvectors (a , b , c) in the same way as Kane, we are assuming that the interactions with higher bands are sufficiently weak that the higher band wave functions are not significantly mixed into the valence and conduction bands over the energy range studied. The alternative to this approach is not actually very difficult, and entails using a larger basis than the eight wavefunctions used by Weiler. We shall just accept that the results may not be very accurate far above the band gap. Since we are also ignoring phonon-assisted transitions, and alloy disorder allowing non-conservation of k , this is not unreasonable.

The absorption coefficient is modified for heavy doping by the Moss-Burstein shift (7) due to the conduction band states becoming populated (or the valence band states depopulated, although the effect is smaller). This is easily taken into account by multiplying the absorption coefficient found for undoped material by the probability that the appropriate states are occupied. Kane's equation 35 and 36 taken together become

$$\alpha = \frac{8\pi^2}{3} \frac{P^2 \alpha_c}{nh\nu} \sum_j B_j \rho_j(E) (1-f_c(E)) f_j(E) \quad (4)$$

Here $f_c(E)$ and $f_j(E)$ are the probability that the electron and hole states are populated with electrons and

$$B_j = (a_c c_j + c_c a_j)^2 + (a_c b_j - b_c a_j)^2 \quad (5)$$

Equation 4 has been written in terms of the fine structure constant α_c (subscripted to minimise confusion with the absorption coefficient). This allows one to use any system of units which is familiar, since α_c is dimensionless. The populations $f_c(E)$ and $f_j(E)$ are given by Fermi-Dirac statistics once the Fermi energy is known.

The Fermi energy can be determined quite easily without approximations. For degenerate material, it is first calculated assuming that the carrier concentration (n_e) is equal to the doping level, using E-k curves from the Hamiltonian and the density of states in k-space.

$$k_F^3 = 3\pi^2 n_e \quad (6)$$

This is the Fermi wavevector at low temperature. This is then refined by including the minority carrier concentration and the effects of finite temperature near the Fermi level. This procedure converges rapidly for degenerate material, and can be made as accurate as is required. For material with the Fermi level near the band edge, the iterative procedure has been adapted in an ad hoc way to improve convergence.

Other necessary inputs to the calculations are the carrier concentration from Hall effect measurements, the x-value of the material from EDAX, and the temperature and x dependence of the band gap (8).

Before embarking on detailed calculations, it is worth considering how sensitive this theory is to the input parameters. We consider two points: the magnitude of the absorption coefficient, and the Moss Burstein shift.

It is easy to show that the magnitude of the absorption coefficient is nearly independent of the heavy hole mass, and varies approximately as $1/P$. Once E_g is chosen, P is the only remaining parameter with a significant effect on the form of the curve. It is worth noting that in the early days of semiconductor work, P^2 was often considered as constant for all materials, so that P cannot be considered as a free parameter. The reason for this is fairly fundamental in pseudopotential theory, where P is closely linked to the lattice parameter. In other words the form of the absorption edge is not very adjustable: if a material obeys k.p theory, then the data should fit reasonably well. It seems on the basis of limited data that good agreement with theory is found for CMT (9). In some cases (2,10) the differences between theory and experiment have their origins in incorrect theory.

The Moss-Burstein shifted absorption edge in heavily doped material is a measure of the temperature dependence of the gap between valence and conduction bands at the Fermi wavevector k_F , which is directly linked to n_e (eq 6). If proper account is taken of second order effects (eg the spread in energy of carriers at high temperature and the presence of minority carriers) then, in principle at least, it is possible to map out the dependence of the band gap on k using suitably doped samples. Note that we do not make reference to the absolute magnitude of the Moss-Burstein shift, which could include band gap narrowing terms, uncertainties in electrical measurements, etc. Since it is known that the band gap only has a positive temperature coefficient for alloys with low E_g , and the higher gaps seen in reflectance behave normally, it is tempting to identify the anomalous behaviour of the E_0 gap as occurring only at low energies. If this is so one might expect a dependence of E_F on temperature which varies in the same way as that of E_g , with zero temperature coefficient for values of $E_F \sim .6\text{eV}$. This would mean that P would have to vary with temperature within the k.p description. This might not be the correct way of looking at the problem, however. Consider two possible mechanisms for the anomalous temperature dependence of the gap, which have not previously been considered. One is mixing with high lying core wavefunctions, like the Hg d-orbitals. This is known to be responsible for anomalous temperature dependences in the copper and silver halides, and in a range of other Cu and Ag tetrahedrally bonded semiconductors (11,12). The change in the hybridisation with temperature would then (roughly speaking) shift the valence band rather than the conduction band, and the Fermi energy would behave in the same way with temperature as the band edge. The contribution of the change in hybridisation with temperature to a changed value of P would (hopefully) be relatively small.

The second possible mechanism involves some extra coupling between valence and conduction bands which is not included in k.p theory. This would have to involve some

characteristic not found in InSb, whose temperature behaviour is normal. An obvious possibility is some form of acoustic phonon assisted alloy scattering. This would mix valence and conduction bands thermally, and would appear off-diagonal in the Hamiltonian, in the same way as the $k.p$ term, but have no k dependence. This would effectively change the form of the Hamiltonian, and could be arranged, for example, to shift the band edge significantly with temperature, but have little effect near k_F . This explanation would fail to explain the temperature dependence of E_0 in HgTe, however.

Neither of the above mechanisms has been worked out: they are presented as examples of the different sorts of model which the present experiments might hope to resolve.

So far, the theory outlined has been conventional. There is one further approximation involved that we should like to explore, which is not normally mentioned in this context. This is the dispersion in the refractive index. Since the refractive index appears in the expression for the absorption coefficient, if the refractive index varies with photon energy, then so must the absorption coefficient.

Equation 4 actually gives ϵ_2 , the imaginary part of the dielectric constant. The refractive index appears in order to convert this to an absorption coefficient.

$$\alpha = \frac{\omega \epsilon_2}{cn} \quad (7)$$

where ω is the angular frequency, c the velocity of light and n is the refractive index (not to be confused with the carrier concentration).

The real and imaginary parts of the dielectric constant are related through the Kramers-Kronig relations (13).

$$\epsilon_1 - 1 = \frac{2}{\pi} \int_0^{\infty} \frac{\epsilon_2 \omega}{\omega^2 - \omega_0^2} d\omega \quad (8)$$

so once the spectrum of ϵ_2 is known, that of ϵ_1 can be calculated and the absorption coefficient and refractive index deduced using

$$n = \left[\epsilon_1 + \left[\epsilon_1^2 - \epsilon_2^2 \right]^{1/2} \right]^{1/2} \quad (9)$$

with equation 7.

The above presumes the spectrum of ϵ_2 is known for all frequencies. This is of course not so, but it is reasonable to assume that the contribution of higher bands can be taken in to account using a constant contribution to ϵ_1 , and transitions between the top valence bands and lowest conduction band are the only ones which need to be integrated over explicitly. This integral is formally divergent for large ω , but this only means that the theory does not work for very large energies, where the inclusion of higher bands by perturbation theory is not valid. Provided the integral is truncated well above the region of interest, results for the dispersion independent of the value chosen for the upper limit are obtained. The constant contribution of higher bands needs to be adjusted if the upper limit of integration is changed, and we choose to fit the refractive index well below E_g to a value of ~ 3.5 for $x = .2$ material (14). The refractive index below E_g is expected to change with x and with heavy doping; these changes are taken into account by the present theory by choosing a constant contribution from higher bands of $\epsilon_1 = 11$ if the integral is truncated at a photon energy = .8eV.

This theory is simple and standard. A different approach has been advanced by Jensen and Torabi (15), which results in an apparent divergence in the refractive index near E_g . This is unexpected, but it is not possible to comment on whether the theory might be correct away from the band gap because it is so complicated.

RESULTS

The main result of this work is a programme which can be used to calculate the absorption of narrow gap semiconductors with confidence that no significant approximations have been made except for the neglect of hole anisotropy ($\gamma_3 - \gamma_2 = 0$), and the inclusion of remote bands empirically through perturbation theory (the values chosen for γ_1 , γ' and F). The parameters used are Weiler's (5), with a value of γ' guessed at .5, somewhere between γ_2 and γ_3 and are listed in table 1. They give a heavy hole mass of .44 m_0 . (This is a parameter to which the absorption is not very sensitive).

Examples of the results are shown in Figs 1 - 6, compared with calculations using Anderson's approximate theory with the same heavy hole mass and matrix element. Figure 1 shows plots of energy against k^2 , which demonstrates how marked the non-parabolicity is, and that the effect of Anderson's approximations is to underestimate the non-parabolicity at large k . Near threshold, the approximate solutions are quite accurate. This is in fact due to a cancellation between the effects of assuming infinite spin orbit splitting and ignoring the effects of higher bands: if the spin-orbit splitting alone is included in the more exact theory, the agreement with Anderson is much worse.

Fig 2 shows that the absorption is almost entirely due to transitions from the heavy hole band, so that errors in the light hole dispersion are not important. The approximate theory works well within about .2eV of threshold. Outside this range, the accuracy decreases rapidly. For infra-red detector calculations, however, the important region can be treated satisfactorily with the approximate theory.

Fig 3 shows the absorption for three different values of band gap for low doping at low temperature. Fig 4 shows for comparison the effect on the absorption edge of doping the material with 10^{18} donors at 77K. Note that there are two distinct thresholds in the absorption which correspond to the shifted edges for transitions from the two valence bands. The Moss Burstein shift calculated using approximate theory is only slightly in error (a few meV).

Figs 5 and 6 show the dispersion of the refractive index for the region near E_g and a comparison of the absorption calculated with dispersion with that obtained using a constant refractive index. Clearly the effect of the dispersion on the absorption coefficient is fairly small, both for doped and undoped material. The dispersion should be taken into account in fitting interference fringes in thin detectors, however.

EXPERIMENT

The samples used were grown by Te rich liquid phase epitaxy, and were doped with Al. Two pieces of the same slice (ALP 107) were used, one as grown, and the other had been annealed at 250°C for 48 hours under Hg saturated conditions. The top surface of both samples had been etched. Hall effect measurements gave low temperature electron concentrations of $8.10^{17} \text{ cm}^{-3}$ (as grown) and $3.5.10^{18} \text{ cm}^{-3}$ (annealed). The layer thicknesses were slightly uncertain; these carrier concentrations were deduced by adjusting the thicknesses of the samples to give an approximate fit to the absorption data. The x value was $\sim .3$. The band gap and Fermi energies deduced from these parameters are listed in table 2. Transmission measurements were made at room temperature and 77K using a double beam spectrometer. Residual imbalance between the beams was removed by ratioing with spectra taken without a sample. Sample size and roughness precluded absolute measurements, but the free carrier absorption is sufficiently weak that there is little difficulty in fixing a baseline empirically. The absorption edges shown are sharper at low temperature than at room temperature as expected, but show a clear shift to lower energy on cooling. There is quite good agreement between the calculated and experimental spectral at room temperature, but no so for the 77K curves, which are significantly broader than the predicted curves, suggesting that sample non-uniformity could

be a problem. Modelling shows that the gradient of x with depth in the layer expected is far too small to account for the width of the 77K spectra. It may be that microscopic disorder is responsible, or broadening associated with the screening by the free electrons.

Measurements of the Moss Burstein shift in CMT have been reported by Dingrong et al (16), but do not go to high enough absorption coefficient values to permit a comparison with the present results. Their data at $\alpha = .01 \mu^{-1}$ show a shift to higher energy on cooling, in agreement with theory, but outside the range of accuracy of the present results.

CONCLUSION

It has been shown that Anderson's approximations to k.p theory do not introduce serious errors on the calculated optical absorption near threshold. This is due to a cancellation of errors, which is somewhat fortuitous. The Fermi energies calculated for degenerately doped material are also good. No firm conclusion has been reached with the data available at the time of writing on the temperature dependence of the band parameters.

ACKNOWLEDGEMENTS

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Note that the dispersion in refractive index near E_g is probably overestimated by simply using peak positions of the interference fringes, as the authors seem to have done, without allowing for the absorption in a full calculation.
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FIGURE CAPTIONS

1. Dispersion curves for CMT with $E_g = .1\text{eV}$ given by Weiler's Hamiltonian with the parameters of Table 1, and Anderson's approximation to it.
2. Absorption due to transitions from the light hole band (l.h) and the heavy hole band (h.h), and their sum (total) given by the approximate and 'exact' theories for $E_g = .2\text{eV}$ and low doping and temperature.
3. Absorption curves for three different band gaps from the approximate and exact solutions for low carrier concentration and temperature.
4. As fig 3, but with $N_d = 10^{18} \text{ cm}^{-3}$ and at 77K showing the Moss-Burstein shift of the absorption edge.
5. Refractive index dispersion for two different dopings ($N_d = 10^{15} \text{ cm}^{-3}$ and $N_d = 10^{18} \text{ cm}^{-3}$) for material with $E_g = .2\text{eV}$. The calculations are uncertain to within a constant, which has been chosen to match (roughly) the data of (14).
6. Absorption curves for the sample of Fig 5 with and without the varying refractive index.
7. Theoretical and experimental absorption curves for as grown and annealed material (sample ALP107) at room temperature and 77K.

TABLE 1

Parameters used in the calculations

P	$8.5 \cdot 10^{-8}$ eV cm.
Δ	1eV
n	3.5
γ_1	3.3
γ'	.5
F	-.8

TABLE 2

Fermi energies deduced for the samples used.

T (K)	E_g (eV)	N_d (cm^{-3})	$E_f - E_c$ (eV)
77	.243	$8 \cdot 10^{17}$.127
293	.289	$8 \cdot 10^{17}$.098
77	.243	$3.4 \cdot 10^{18}$.231
293	.289	$3.4 \cdot 10^{18}$.211

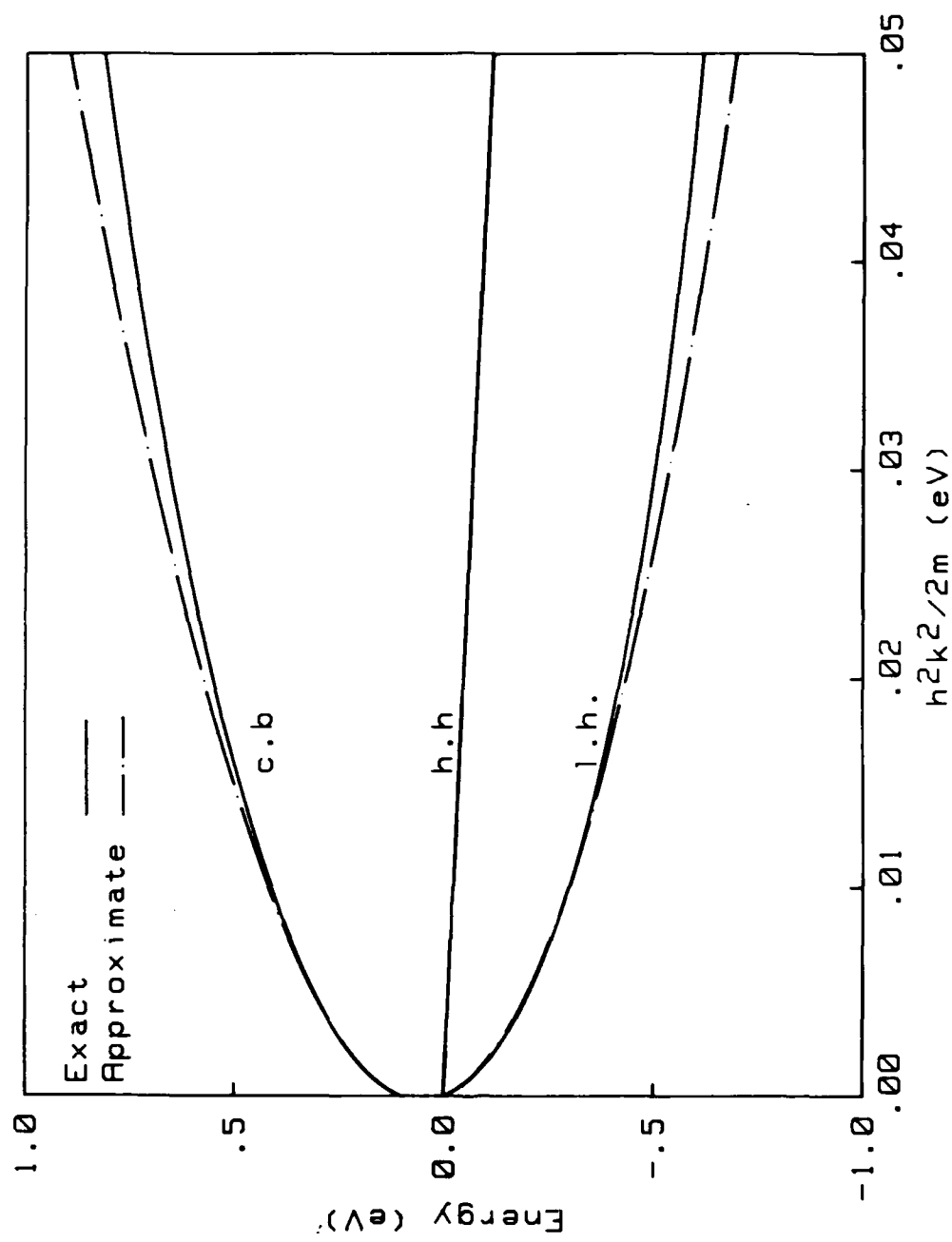


Fig. 1

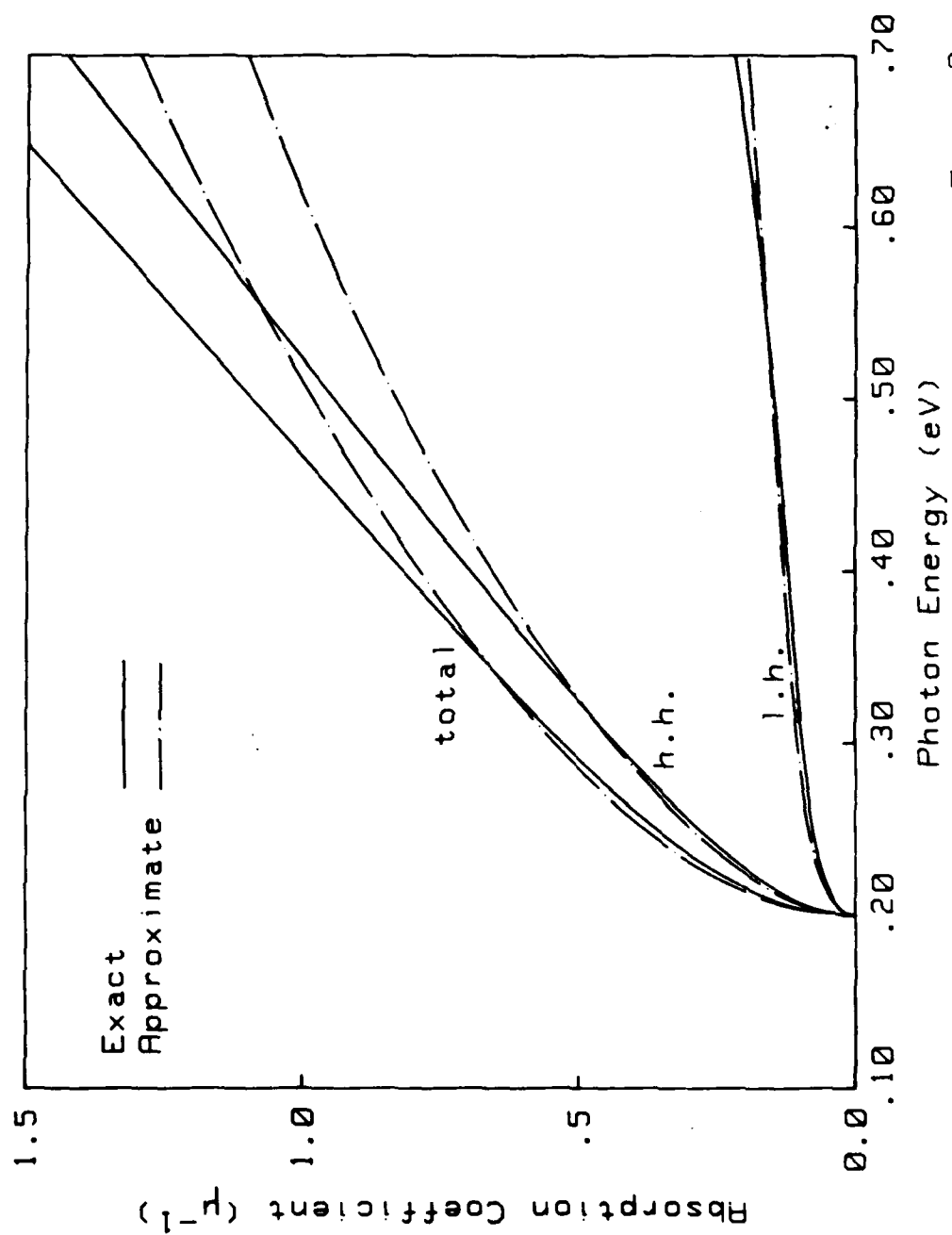


Fig. 2

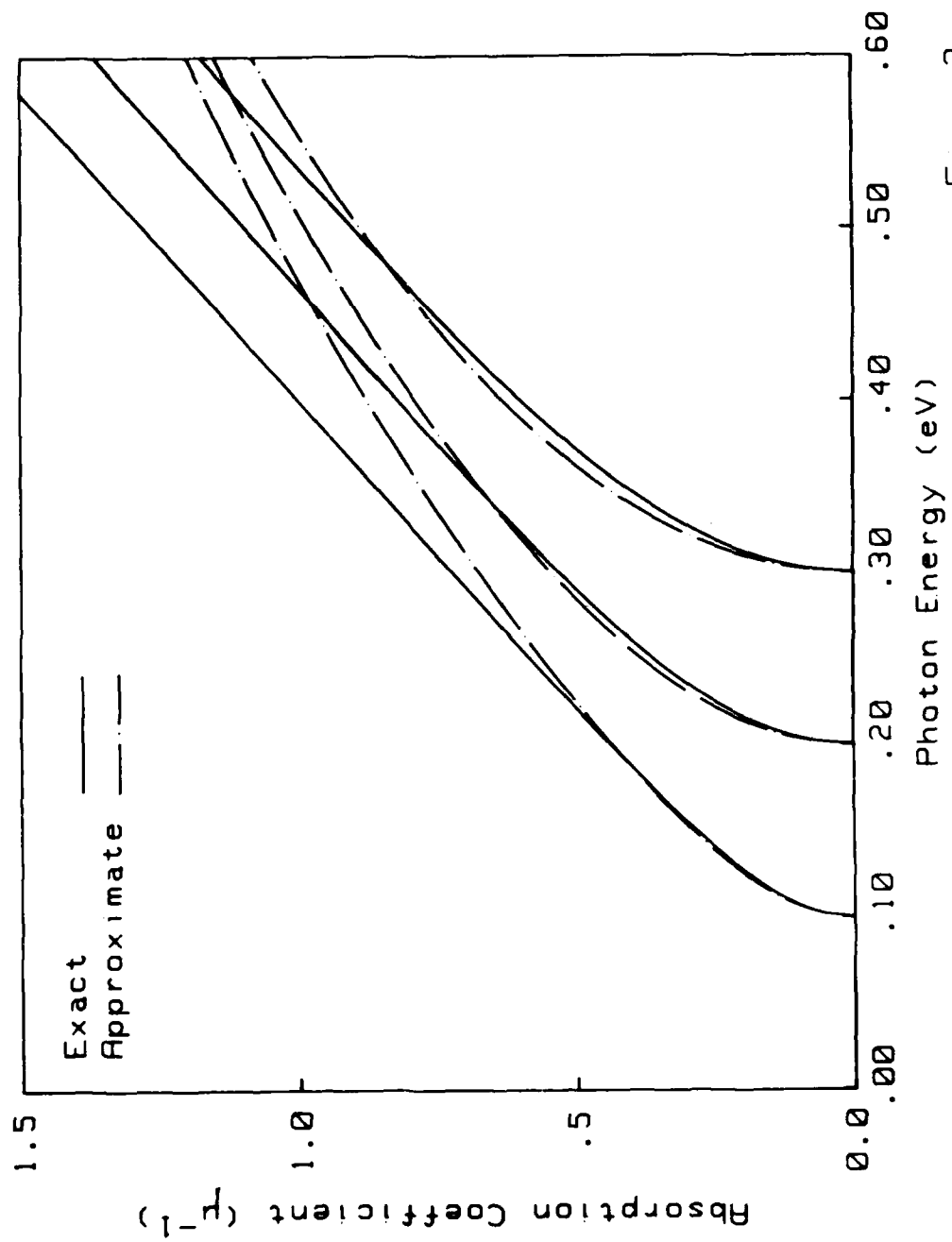


Fig. 3

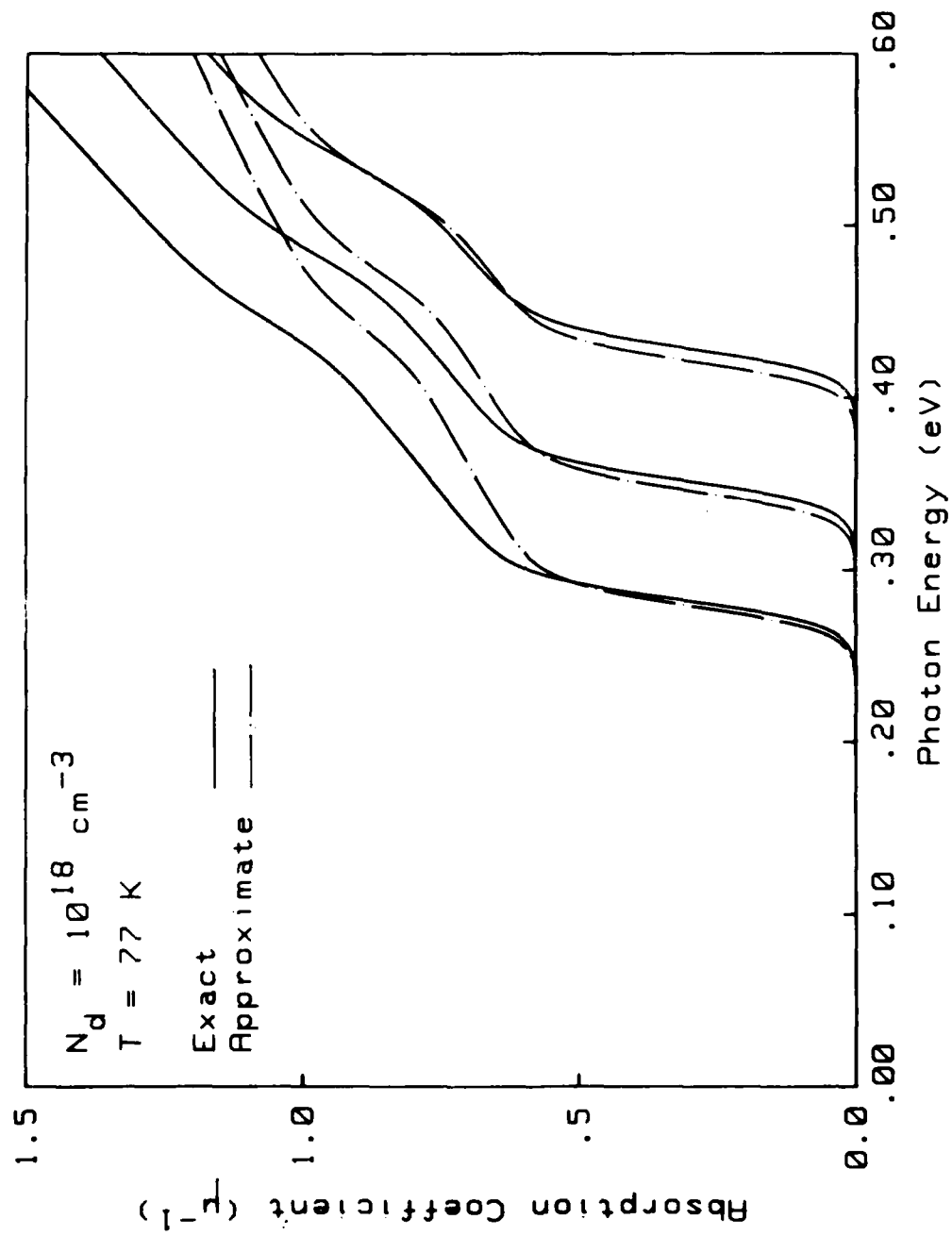


Fig. 4

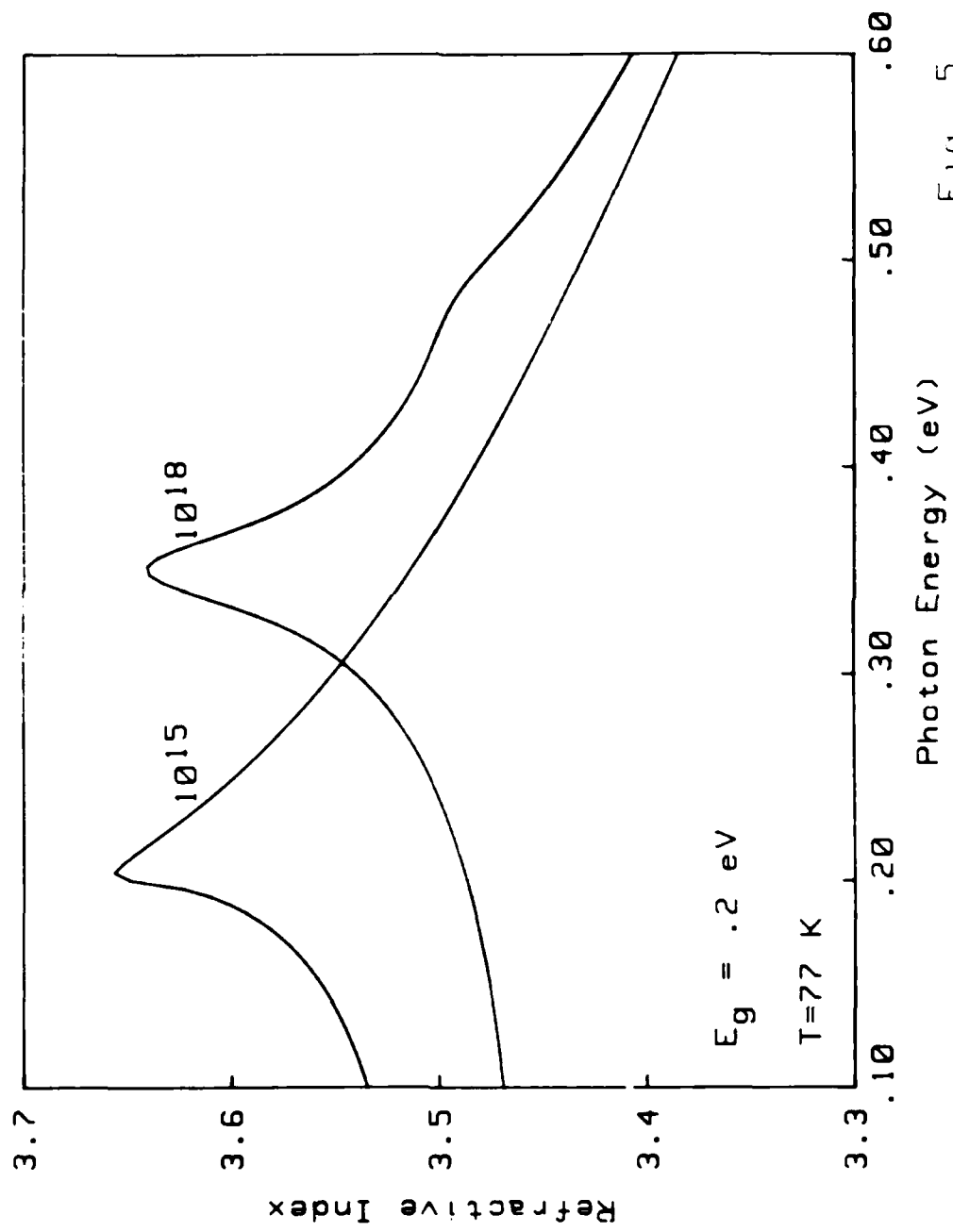


Fig. 5

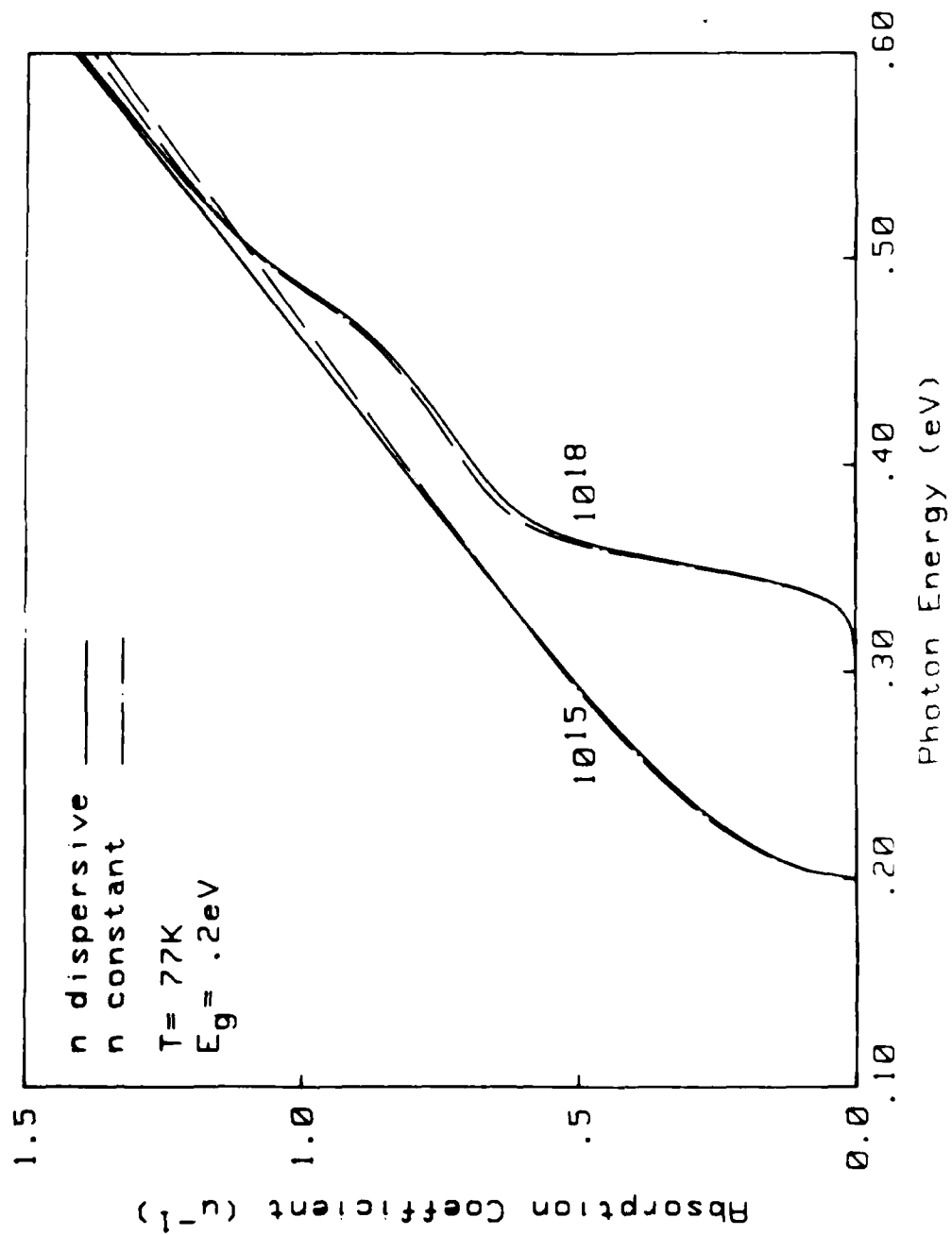


Fig. 6

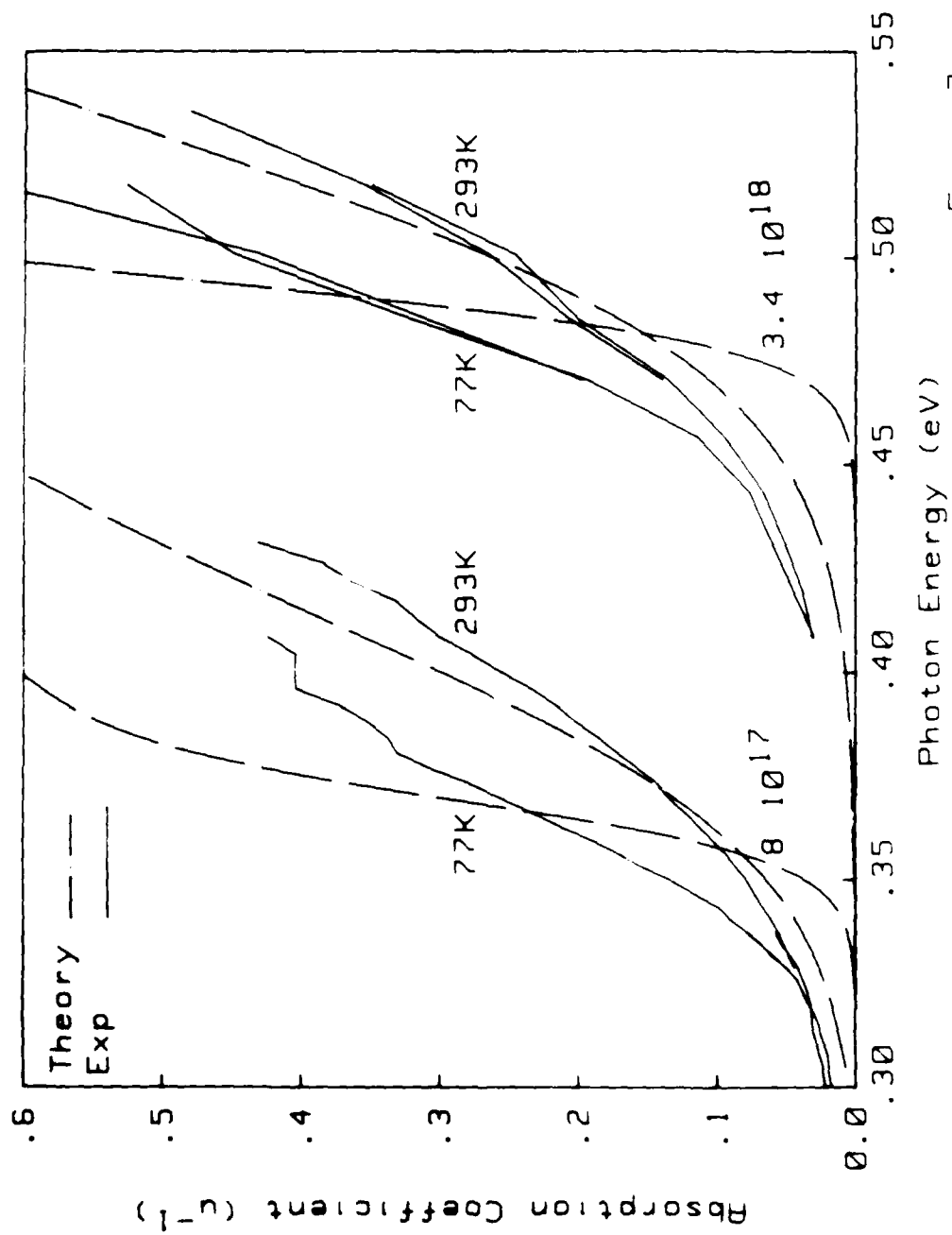


Fig. 7

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Abstract The theory of optical absorption is heavily doped (degenerate) CMT is formulated to make use of the most recently measured band parameters. The absorption theory is compared with Anderson's approximation to Kane's k.p. theory. The differences are found to be small near threshold, due to a somewhat fortuitous cancellation of errors. The dispersion of the refractive index near the band gap is calculated. This has only a small effect on the calculated absorption, but could be of importance in modelling interference fringes in thin detectors.				

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